Experimental report

29/10/2019

Proposal:	**9-11-1853**	**Council:**	4/2017
Title:	STRUCTURAL STUDIES ON SYNDIOTACTICPOLYSTYRENE / POLY(3-HEXYL THIOPHENE) COMPOSITE		
Research area:	Materials		

This proposal is a new proposal

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Samples: sPSH (C_8H_8), sPSD (C_8D_8), P3HT ($C_{10}H_{14}S$), p-xyleneD (C_8D_{10})

Instrument	Requested days	Allocated days	From	To
D11	1	1	22/10/2018	23/10/2018

Abstract:

Composites composed of syndiotactic polystyrene and Poly (3-hexyl thiophene) have been prepared by making a hybrid thermoreversible gel in p-xylene. We expect to obtain a novel material with enhanced photo-physical properties. The composites have been characterized with UV-Vis and XRD studies. Morphological studies reveal the presence of fibrillar network in the gel. Absorption studies show the presence of vibronic bands that are indicative of formation of P3HT nano-aggregates within the sPS matrix. The issue remains unanswered about the place where P3HT chains are individually located inside sPS crystalline lattice, thus generating a molecular compound, or simply forming fibrils that pervade the sPS gel. By using appropriate labelling (deuterated syndiotactic polystyrene and deuterated p-xylene) we expect to determine the structure of the hydrogenousP3HT moiety.

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In order to determine directly the P3HT chain structure within the sPS gel small angle neutron scattering (SANS) studies were performed (25°C, 40°C and 60°C). In order to match the coherent scattering of deuterated sPS, a solvent mixture of CyclohexaneD/*p*-XyleneD (70: 30, designated as solventD in what follows). Under these conditions, only the P3HT moiety produced a coherent scattering.

Results are reported in **Figure 1** with a Kratky-plot ($q^2I(q)$ vs q). The scattered intensity is virtually the same for the pure P3HT and for the P3HT in the composite in the low-q range, typically for $q_c< 1.3 nm^{-1}$. While the data reach a constant value in the case of pure P3HT for $q> q_c$, namely $I(q)\sim q^{-2}$, a conspicuous departure from this behaviour is observed for the P3HT in the case of the P3HT/sPSD gel, particularly for the highest P3HT concentration. It is known that P3HT crystallizes from solutions under the shape of very long crystalline ribbons. Yet, one should keep in mind that a significant fraction of the P3HT chains are not incorporated into these ribbons, and thus remain in solution. If they possess a Gaussian statistics, then they scatter like $I(q)\sim q^{-2}$ as is seen for the mixture P3HT/solventD. Therefore, it is assumed that the $I(q)\sim q^{-2}$ at large q arises essentially from the non-incorporated chains as the ribbons scattering rapidly reaches zero. For determining the characteristics of the only P3HT ribbons, one can further subtract this intensity from the total intensity as shown in **Figure 1c**. The data can then be fitted with the equation developed by Mittelbach and Porod [1] for long ribbons of rectangular cross-section of length a and width b (a<b):

$$q^2I(q)\sim \frac{2q\mu_L}{\pi}\int_0^{\pi/2}\left[\frac{\sin qa/2\cos\theta}{qa/2\cos\theta}\times\frac{\sin qb/2\sin\theta}{qb/2\sin\theta}\right]^2\sin\theta d\theta \quad (1)$$

The initial behaviour 1/q seen by plotting Log I(q) vs Log q confirms that one is dealing with straight objects in both systems. From 1 one then derives a= 5nm and b=25 nm, the value of b being in good agreement with electron microscopy findings.

The fit is also valid for the P3HT/sPSD gel up to $q= q_c$. Conversely, for $q> q_c$ the intensity can be fitted at this level of resolution with a model developed for a solid cylinder wherein the extended P3HT chain of large persistence length (rigid chain) can be inscribed. For a cylinder of cross-sectional radius r, and a mass per unit length μ_l, the intensity reads[2]:

$$q^2I_{abs}(q) = 4\pi q C_{P3HT}\mu_L\times\frac{J_1^2(qr)}{q^2r^2} \quad (2)$$

The fit yields r= 0.4±0.05 nm which suggests only one P3HT chain where the aliphatic moieties are extended. The mass per unit length is found to be μ_l= 200±20 g/nm×mole, while the actual value should be about 430 g/nm×mol if one considers one rigid chain. This discrepancy can simply be accounted for by considering that the P3HT fraction of extended chains represents only about 1/2 of the system. The composite therefore contains a significant fraction of non-aggregated P3HT chains that definitely differ from those remaining in solution.

The mass per unit length of the ribbons it is found to be $\mu_L\approx 9.3\times10^4$g/nm×mol, which is the right order of magnitude for a ribbon of rectangular cross-section 5×25 nm^2 (about 8.6×10^5 g/nm×mol).

Conversely, experiments performed at 60°C reveal a change of behaviour (**Figure 1d**), corresponding to the melting (for C_{P3HT}= 0.005 g/cm^3 and 0.008 g/cm^3) or the onset of melting (for C_{P3HT}= 0.012 g/cm^3) of the P3HT ribbons. Again, the behaviour at larger q of the P3HT moiety differs drastically between pure P3HT network or P3HT/sPSD network. For the latter case, the intensity can again be fitted with modified equation 2 by including a constant term that stands for the fraction of disordered chains:

$$q^2I_{abs}(q) = 4\pi q C_{P3HT}\mu_L\times\frac{J_1^2(qr)}{q^2r^2} + Const$$

As above, the fit yields a cross-sectional radius r= 0.4±0.05 nm, and a mass per unit length μ_l= 207±20 g/nm×mole.

Clearly, these outcomes point to the existence of a significant fraction of extended P3HT chains that are linked in a way or another to the unmolten sPSD fibrils. They may be encapsulated inside the sPS fibrils and/or be deposited onto the fibrils surface. That these chains are isolated rather points to encapsulation. Indeed, if the P3HT chains had stuck onto the sPS fibrils surface one would expect them to further aggregate.

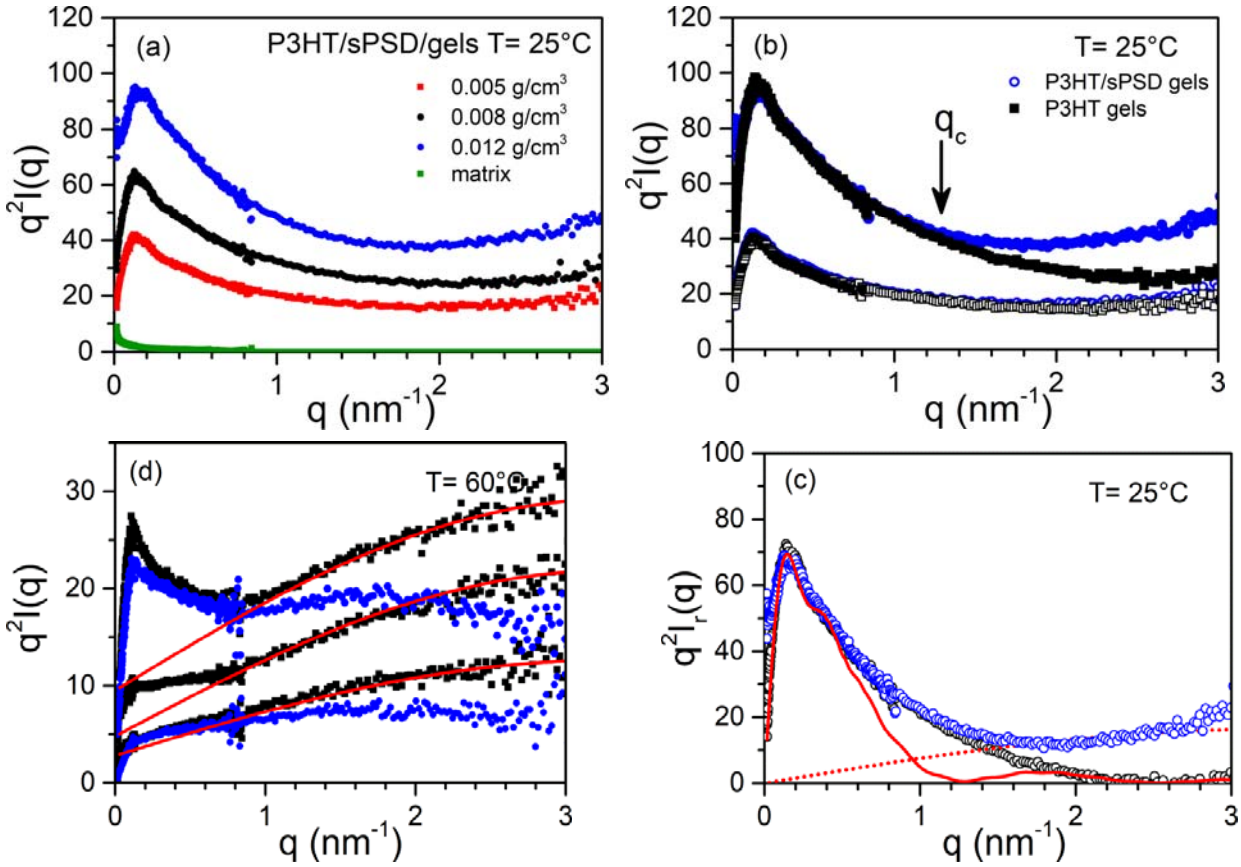

Figure 1. Neutron scattering data plotted by means of a Kratky-plot, q2I(q) vs q: **(a)** P3HT/sPSD/solventD, from top to bottom C_{P3HT}= 0.012 g/cm^3, 0.008 g/cm^3, 0.005 g/cm^3; the green curve stands for the residual coherent sPSD background of the sPSD/solventD matrix after subtraction of the intensity scattered by the solventD mixture; **(b)** comparison between P3HT/sPSD/solventD (blue symbols), and P3HT/solventD (black symbols). **(c)** Here the curves have been obtained after subtracting a q^{-2}signal corresponding to the free, disordered P3HT chains, in both cases C_{P3HT}= 0.012 g/cm^3 with ○= P3HT/sPSD/solventD; ○= P3HT/solventD; the solid red line is a fit with a ribbon of rectangular cross-section a= 5nm and b= 25nm, the red dotted red line is a fit with a solid cylinder of cross-sectional radius r=0.4 nm.; (d) data obtained at 60°C for (●)= P3HT/solventD, and (●)= P3HT/sPSD/solventD, red solid lines are fits with equation 7.

These results will be soon published in Macromolecules (http://dx.doi.org/10.1021/acs.macromol.9b01512)

References

1. Mittelbach, P. *Acta Physica Austriaca*, **1964**, *19*, 53-57
2. Fournet, G. *Bulletin de la Société Française de Minéralogie et Cristallographie*, **1951**, *74*, 39
3. Mittelbach, P., Porod G. **1961**, *14*, 185